MEMORANDUM

TO: Nancy McClintock, ERM Division Manager

FROM: Robert Hansen, Bioassessment Project Manager

Re: Nitrogen isotope study of Barton Creek

DATE: MAY 3, 1994

Dear Nancy:

The Water Research and Evaluation Section (WRE) of ECSD recently conducted a nitrogen stable isotope study along the reach of Barton Creek that was impacted by algae blooms in 1992 and 1993. Based on the unique isotopic signature of many nitrogenous compounds, this research method has proven extremely valuable in identifying and tracing potential and suspected sources of nitrate contamination in surface and groundwaters. Samples of both algae and water were collected from tributaries and mainstem sites and analyzed by Coastal Science Laboratories in Austin, Texas for natural abundance values of ^{15}N. The ratio of ^{15}N to ^{14}N in samples is determined by mass spectrometry and is reported as del ^{15}N (parts per mil). Simply defined, del ^{15}N is the difference between the $^{15}N/^{14}N$ of the sample and the $^{15}N/^{14}N$ of the standard (atmospheric nitrogen). Laboratory data for study sites along Barton Creek are presented in Attachment 1. I have also included a map of the pertinent Barton Creek study site locations.

Nitrogen isotope values increase progressively from upstream to downstream sites. The del ^{15}N value for the upstream reference site directly upstream of the Barton Creek Boulevard bridge was +4.6 per mil. This low value indicates that the creek mainstem above the zone of effluent irrigation is relatively unimpacted by human and animal wastes. At Fazio Tributary the del ^{15}N had risen to +7.1 per mil with local growth of Cladophora having a nitrogen isotope signature of +7.5 per mil. At the confluence of Crenshaw Tributary and Barton Creek mainstem the isotope signature of the mainstem water had increased to an average of +8.9 per mil. These del ^{15}N values indicate that animal waste and sewage effluent contribute an increasing percentage of the nitrogen sink of Barton Creek between Barton Creek Boulevard bridge and Lost Creek Boulevard bridge.

Numerous studies conducted over the past 20 years have reported the nitrogen stable isotope range for animal waste and septic tank effluent to be +10 to +22 per mil. Isotope sampling at the Lost Creek Spring downstream of the Lost Creek Boulevard bridge indicates that sewage effluent is the primary source of nitrogen in the spring discharge. Samples collected at the Lost Creek Golf Course effluent irrigation pond had an average nitrogen isotope signature of +21.0 per mil. Water samples taken directly from the Lost Creek Spring downstream of the Lost Creek Boulevard bridge had an even higher del ^{15}N value of +22.1 per mil. del ^{15}N signatures in this high range indicate that sewage effluent is contaminating the groundwater in this zone. Additional water and algae samples have been collected and are currently being analyzed to confirm these findings. Further studies should be conducted as soon as possible to locate the entry points of the nitrogen contamination in the groundwater system adjacent to and downstream of the Lost Creek Golf Course..

ADDENDUM

TO: Nancy McClintock, ERM Division Manager

FROM: Robert Hansen, Bioassessment Project Manager

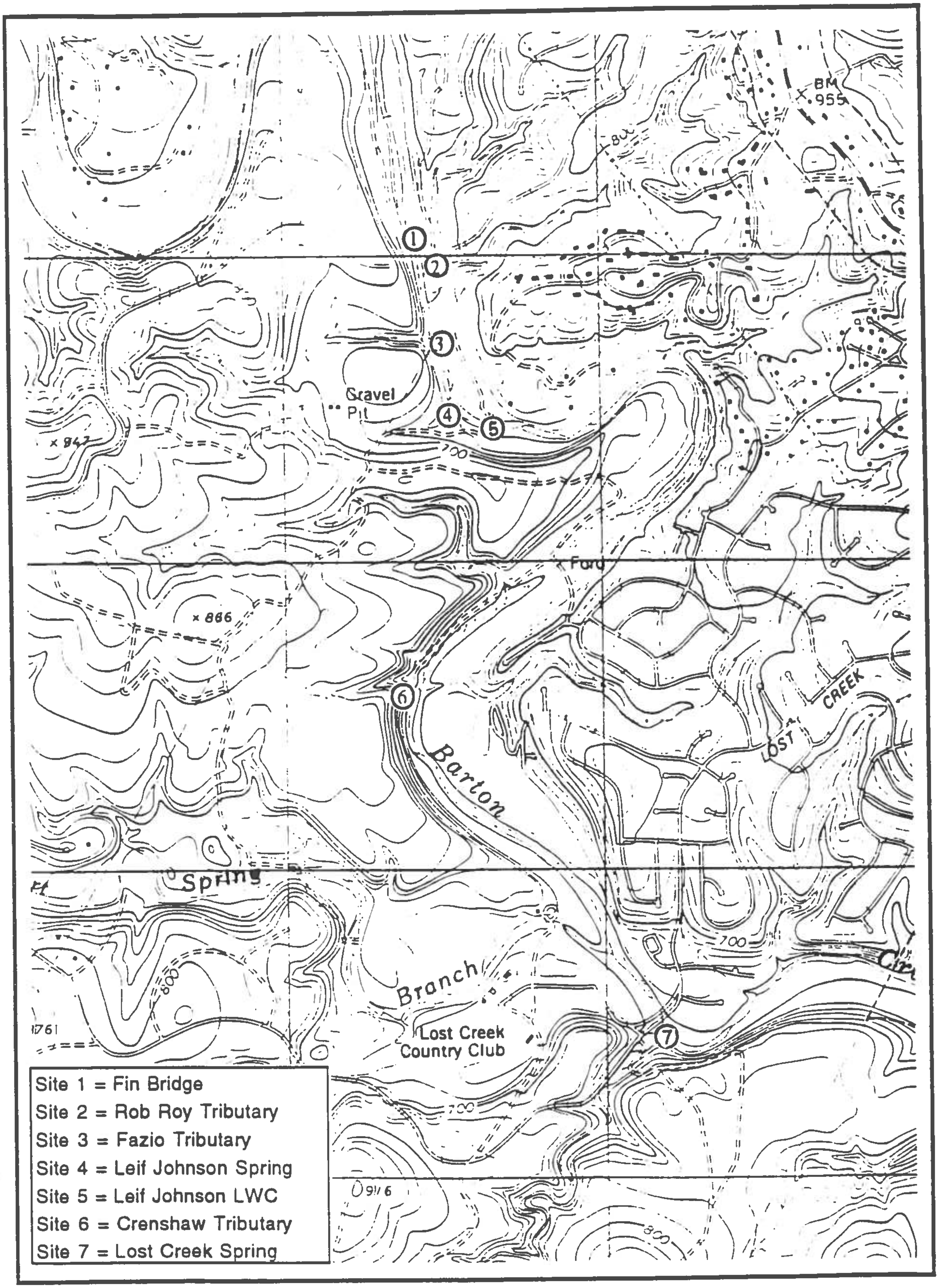
Re: Additional Barton Creek Nitrogen Isotope Data

Date: May 23, 1994

Nancy:

Since you received my original memo (which should have been dated May 3, 1994) concerning the nitrogen stable isotope analysis results for Barton Creek, Coastal Science Laboratories (CSL) has completed the lab analysis of additional water samples that we collected at Lost Creek Spring. These data corroborate the high del ^{15}N values for water samples collected Feb. 24, 1994. CSL reported a del ^{15}N value of +22.1 for the Feb. 24, 1994 sample and an average value of +19.0 for the April 19, 1994 sample. The high values for both sampling dates indicate that animal waste and sewage effluent are the major sources of nitrogen in the spring water and warrant further studies to locate the potential sources of contamination.

Barton Creek Stable Nitrogen Isotope Data			
Date	Site	del 15N	del 15N
2/15/94	Fin Bridge Mainstem	4.6	
2/15/94	Fin Bridge Mainstem Spirogyra	3.1	
2/15/94	Rob Roy Trib.	Ins.	
2/15/94	Rob Roy Trib. Spirogyra	3.6	
2/15/94	Rob Roy Trib. Chaetophora	3.5	
2/15/94	Mainstem at Fazio Spirogyra	2.6	
2/15/94	Fazio Trib.	7.1	
2/15/94	Fazio Trib. Cladophora	7.5	
2/15/94	Mainstem below Fazio Spirogyra #1	0.2	
2/15/94	Mainstem below Fazio Spirogyra #2	3.0	
2/15/94	Leif Johnson Spring #1	6.1	
2/15/94	Leif Johnson Spring #2	7.2	
2/15/94	Leif Johnson Spring (Cladophora?)	3.9	
2/15/94	Leif Johnson LWC Spirogyra	5.0	
2/15/94	Leif Johnson LWC Cladophora	0.3	
2/07/94	Crenshaw Trib.	8.0	9.8
2/07/94	Mainstem below Crenshaw Cladophora #1	5.9	
2/07/94	Mainstem below Crenshaw Cladophora #2	6.0	
2/24/94	Lost Creek Bridge Mainstem	8.5	
2/24/94	Lost Creek Bridge Cladophora	5.9	
2/22/94	Lost Creek Spring	22.1	
4/19/94	Lost Creek Spring	17.7	20.3
2/22/94	Lost Creek Package Treatment Seep	6.8	
2/07/94	Short Spring Branch	6.8	
2/07/94	Lost Creek Residential	7.8	
2/07/94	Lost Creek Golf Course Effluent Pond	20.8	21.2


BM 955
800
Gravel Pit
x 842
700
Ford
x 866
Barton
LOST CREEK
Spring
Branch
Lost Creek Country Club
700
800
700
800
1
2
3
4
5
6
7
Site 1 = Fin Bridge
Site 2 = Rob Roy Tributary
Site 3 = Fazio Tributary
Site 4 = Leif Johnson Spring
Site 5 = Leif Johnson LWC
Site 6 = Crenshaw Tributary
Site 7 = Lost Creek Spring

Barton Creek Stable Nitrogen Isotope Analysis

Date	Site	del 15 N	del 15 N	NH3-N	Ortho-P	NO3-N	pH	TDS
2/2/94	Upland Spring	5.4	5.1	~~0.06~~ 0.07	0.01	~~0.5~~ 1.8	8.2	~~150~~ 170
2/2/94	Upland Spring Spirogyra	0.9	0.6					
2/2/94	Southwest Parkway Spring	22.1	20.9	0.07	0.02	0.4	7.5	300
2/22/94	Hebbingston Hollow Ranch Trib.	10.3	9.8	1.56	0.90	2.7	7.5	380
2/22/94	Hebbingston Hollow School Trib.	1.7		0.13	0.07	0.17	7.8	60
2/22/94	Hebbingston Hollow Mainstem	Ins.		0.02	0.02	0.08	7.7	260
2/22/94	Hebbingston Hollow Spirogrya	4.2						
2/15/94	Fin Bridge Mainstem	4.6						
2/15/94	Fin Bridge Mainstem Spirogyra	3.1						
2/15/94	Rob Roy Trib.	Ins.		0.06	0.01	0.2		
2/15/94	Rob Roy Trib. Spirogyra	3.6						
2/15/94	Rob Roy Trib. Chaetophora	3.5						
2/15/94	Mainstem at Fazio Spirogyra	2.6						
2/15/94	Fazio Trib.	7.1		0.08	0.02	0.2		
2/15/94	Fazio Trib. Cladophora	7.5						
2/15/94	Mainstem below Fazio Spirogyra #1	0.2						
2/15/94	Mainstem below Fazio Spirogyra #2	3.0						
2/15/94	Leif Johnson Spring #1	6.1		0.03	0.01	0.9		
2/15/94	Leif Johnson Spring #2	7.2						
2/15/94	Leif Johnson Spring Cladophora	3.9						
2/15/94	Leif Johnson LWC Spirogyra	5.0						
2/15/94	Leif Johnson LWC Cladophora	0.3						
2/7/94	Crenshaw Trib.	8.0	9.8	0.00	0.03	0.8	7.9	330
2/7/94	Mainstem below Crenshaw Cladophora #1	5.9						
2/7/94	Mainstem below Crenshaw Cladophora #2	6.0						
2/24/94	Lost Creek Bridge Mainstem	8.5						
2/24/94	Lost Creek Bridge Cladophora	5.9						
2/22/94	Lost Creek Spring	22.1		0.00	0.03	2.4	7.4	490
2/22/94	Lost Creek Package Treatment Seep	6.8		0.00	0.05	2.7	7.5	430
2/7/94	Short Spring Branch	6.8		0.06	0.03	0.2	7.9	390
2/7/94	Lost Creek Residential	7.8		0.02	0.03	0.3	7.9	290
2/7/94	Lost Creek Golf Course Pond	20.8	21.2	>2.5	0.90	2.6	9.4	300
2/24/94	Barton Springs Pool (Parthenia)	6.9						
2/24/94	Barton Springs Pool Cladophora	3.6						
	Reference Site H2O							
	Reference Site Cladophora							
	Construction Site Runoff							
	Mainstem above Heb. Hollow Cladophora							
	Mainstem below Heb. Hollow Cladophora							
	Pod 9 H2O							
	Pod 9 Cladophora							
	Lost Creek Trib. H2O							
	Lost Creek Trib. Cladophora							

1. $\delta^{15}N_{air}$ of total inorganic nitrogen in GW ($NH_4^+ + NO_3^- + NO_2^-$)

2. $\delta^{15}N_{air}$ of organic matter (biota) and fertilizers

Nitrogen Isotope Data

SPRING	DATE	AQUIFER	DEL 15 N	DEL 15 N	DEL 15N AVG	TEMP	PH	TDS	NO3-N	NH3-N	ORHTO-P	FECAL C	COMMENTS
				lab duplicate		C		mg/l	mg/l	mg/l	mg/l	colonies/100ml	
Barton Cr Watershed													
Uplands Forked Trib Spring	2/2/94	Glen Rose m3	5.4	5.1	5.25	19	8.2	170	1	0.07	0.01	NT	
Uplands Short Trib Spring	2/2/94	Glen Rose m3	NT	NT		7	8.3	150	0.5	0.06	0.01	NT	
SW Parkway Spring	2/2/94	Glen Rose m3	22.1	20.9	21.5	17	7.5	300	0.4	0.07	0.02	NT	
SW Parkway Spring	4/19/94	Glen Rose m3	15.9	14.4	15.15	23	7.6	300	0.1	0.02	0.07	4	
SWP Spring Alga	4/19/94		17.2		17.2								
Lost Creek Spring A	2/22/94	Glen Rose m2/Terr	22.1		22.1	23	7.4	490	2.4	0	0.03	NT	
Lost Creek Spring A	4/19/94	Glen Rose m2/Terr	17.7	20.3	19	23	7.4	440	2.6	0.01	0.08	1	
Lost Creek Spring B	4/19/94	Glen Rose m2/Terr	11.5	14.2	12.85	23	7.3	460	2.5	0.03	0.1	0	
LCS "B" Alga	4/19/94		12.3		12.3								
Lost Creek PTP Spring	2/22/94	Glen Rose m2/Terr	6.8		6.8	23.5	7.5	430	2.7	0	0.05	NT	
Barton Creek West (Senic B)	5/4/94	Glen Rose m3?	1.0		1.0	22	7.4	610	0.5	0.01	0.02	NT	
Barton Springs	2/3/95	Edwards				22	7.4	290	0.7	0	0.02	NT	Sampled at 10:40 AM
Old Mill Spring	2/3/95	Edwards				22	7.5	310	0.7	0	0.01	NT	Sampled at 11:30 AM
Eliza Spring	2/3/95	Edwards				22	7.4	290	0.6	0	0.02	NT	Sampled at 11:05 AM
BS Edwards Aquifer													
Cold Spring	9/22/94	Edwards	7.3	8.1	7.7	23	7.5	300	1.4	0	0.01	NT	Sampled at 2:25 PM
Backdoor Spring	9/22/94	Edwards	10.7	11.1	10.9	23	7.6	360	1.3	0	0.02	NT	Sampled at 4 PM
Backdoor Spring	2/3/95	Edwards				22	7.6	320	1.1	0	0.06	NT	Sampled at 12:30 PM
Lake Austin Watershed													
Morman Spring	2/3/95	Edwards				23.5	7	430	2	0	0.03	NT	Sampled at 9:50 AM
Mayfield SPring	2/3/95	Edwards				22	7.4	520	0.5	0	0.02	NT	Sampled at 10:10 AM
Bull Cr Watershed													
Developed													
Stillhouse	7/15/94	N Edwards	5.7	7.4	6.55	23	7.2	470	3.1	0.03	0.05	NT	
Barrow	7/15/94	N Edwards	5.7	7.7	6.7	23	7.5	490	4	<0.07	0.05	NT	
Tanglewood	7/15/94	N Edwards	9.1	10.8	9.95	25	7.6	400	1.6	0.06	0.03	NT	
Bull Cr Park Dam	7/22/94	Glen Rose	7.7		7.7	27	7.1	460	2.7	<0.01	0.05	NT	
Bronc	7/22/94	N Edwards	18.1	18.4	18.25	24	7.2	450	2.6	<0.01	0.23	NT	Strong odor
Sierra	7/22/94	N Edwards	8.5	6.8	7.65	23.5	7.5	380	3.7	<0.01	0.05	NT	Strong flow
Sierra (Blind)	7/22/94	N Edwards	5.7	7	6.35								
Schl -2	9/14/94	N Edwards	5.9	5.1	5.5								WWW Lab
Median			6.8		7.18	23.8	7.4	455	2.9		0.05		
Average			8.30		8.58	24.3	7.4	442	2.95		0.08		
Undeveloped													
Pipe	7/15/94	N Edwards/Walnut	3.9		3.9	23	7.6	210	0.9	<0.07	0.01	NT	Flow lower than usual
Buzzard	7/15/94	N Edwards	2.1	3	2.55	22	7.7	250	0.09	<0.07	0.01	NT	Lots of ants
Pit*	7/15/94	Glen Rose/Alluv	7.6	7.1	7.35	28	7.8	270	0.1	0.02	0.04	NT	Lots of ants
Powerline	7/22/94	N Edwards	7.5		7.5	24	7.5	340	0.1	<0.01	0.05	NT	
Plum	7/22/94	N Edwards	3.3		3.3	24	7.5	300	0.5	0.02	0.04	NT	Lots of ants
Median			3.9		3.9	24.0	7.6	270	0.1		0.04		
Average			4.88		4.92	24.2	7.6	274	0.34		0.03		
Miscellaneous													
MoPac Runoff**	7/14/94	None	11.1	11.3	11.2				0.21				
COA Water**	7/14/94	None	1.8	4.7	3.25				0.8				

* Sample from pool in channel

** Artificial rain on MoPac at 35th Street; COA water from tap on site

3 liters = sample size   lab = Coastal Science Labs in Oak Hill

(6 springs not in yet)

Spring water   26 springs (some twice) (6 data pt. not in yet)

algae (2 samples)

7 in BS/EA

9 in Glen Rose

MoPac Runoff
COA water } from you?

10 N. Edwards

>10 ⇒ wastewater

THE STABLE NITROGEN ISOTOPE IN ALGAE BIOMASS IN STREAMS AS AN INDICATOR OF SOURCES OF NITRATE IN THE WATERSHED

PROBLEM STATEMENT

Many researchers have attempted to identify the source or sources of nitrate in streams using various geochemical and isotopic methods as signals for sources such as atmospheric nitrate, natural decay of organic matter, ground water, fertilizer runoff, sewage discharge, or animal wastes. These approaches have met with limited success owing to poor characterization of chemical or isotopic signatures of the sources, mixed sources of nitrate, and the temporal variability of the discharges and loading of nitrate in some watersheds. Good chemical and isotopic characterization of the sources of nitrate have proven successful in some studies, however. Recent applications of both nitrogen and oxygen isotopic signatures of the nitrate anion (C. Kendall, USGS-WRD, pers. comm.) promises to be useful in source identification where land use may produce large loads of nitrate to streams.

In watersheds where the nutrient nitrate is elevated from one or more point or non-point sources, abundant growth of various types of algae may occur in the flowing streams. This growth is likely to be greater than normal from the large input and aquatic transport of nitrate through the tributaries. In urban and suburban watersheds, multiple sources of nitrate both natural and anthropogenic may contribute to large algal blooms in flowing streams that begin in the early part of the growing season and continue for several months until the streamflow ceases or until freezing weather occurs. Seasonal factors will also affect the rate of growth of the algae. These growth factors suggest that algal species that derive their accelerated growth from elevated nutrients such as nitrate in the water column or on sediment may be useful as biological integrators of stream nutrient water quality. More specifically, the species of algae, ***chlodaphora*** for one, biochemically process nitrate with a specific isotopic signature that may be preserved in the biomass. Thus it should be possible to measure the nitrogen isotopic signature of an individual algal species where excessive growth has appeared and relate that information to possible sources of the elevated nitrate in the watershed. Excessive algal growth in a stream is already considered a qualitative measure of diminished water quality. Measurement of nitrogen isotopic signatures in the algal biomass may add to its usefulness in assessing the overall health of a stream. Further tracing of the nitrogen isotope in the food chain may be possible by measuring N-15 in vertebrates and invertebrates that feed almost exclusively on the algae. Longer-lived species whose life cycles exceed that of the algae may be even better long-term integrators of the nitrate source(s).

In most biological processes involving isotopes, there is usually a preference for the lighter isotope in the metabolism that fractionates the isotopic ratio from the reservoir source to the organism. In the case of algal processing of nitrate, some fractionation is suspected, but the magnitude is not known, although presumed to be about 2 per mil (M. Fogel,.Carnegie Inst., pers. comm.), and has not been considered significant in the few studies of nitrogen isotopic uptake by algae. Research conducted on nitrogen isotopic cycling in the stream-algal relationship can determine the apparent fractionation factor from N-15/N-14 ratios in water to N-15/N-14 ratios in algae, although the algae determination should be species-specific as different organisms may have different levels of fractionation (if any). Algae that fix nitrogen from atmospheric nitrogen, such as blue-green algae must necessarily be excluded from this research. Further, the research should carefully measure the nitrate and isotopes in water, sediment, and from the various sources in the watershed.

In central Texas where Cretaceous age limestones dominate, and the topography is hilly, watershed response to rainfall is relatively rapid, especially in developing areas of urban and suburban land uses. Further, spring-fed baseflow to many of the streams also produces rapid storm response. Rapid growth in suburban Austin, Texas has altered land use from natural oak and cedar growth to large percentages of impervious cover and roads, suburban homes, golf courses, and local sewage treatment facilities and septic tanks. Many of these land uses have caused increases of nitrate in streams that enter the two lakes in Austin, one of which, Lake Austin, is the water supply for the City. Algal blooms have been observed in most of the tributaries, and even in Barton Springs, a popular swimming and park area whose water quality is threatened by controversial suburban development in the watershed. The City of Austin has expressed an interest in determining nitrate sources and has supported and is currently supporting watershed studies dealing with this issue.

A team of researchers, including an isotope specialist (Dr. Carol Kendall, USGS-WRD, Menlo Park, CA), a geochemist (Dr. Roger Lee, USGS-WRD, Austin, TX), and an aquatic biologist specializing in algae (to be named), will be assembled to develop the methods and carry out the project of approximately 3 years. Potential cooperators include the City of Austin and the Lower Colorado River Authority.

OBJECTIVE

The objective of this research is to determine the relation between nitrogen isotopic content of various benthic algal species in receiving streams and nitrogen isotopic content of nitrate derived from various land uses and sources in the watershed for the purpose of utilizing excessive algal growth as a short-term integrator of stream water quality. Secondary objectives include determination of fractionation factors of the N-15/N-14 ratios from algal uptake of nitrate, and the determinations of nitrogen isotope content in any vertebrates or invertebrates that feed on the algal species studied that may be useful as longer-term integrators of stream water quality.

APPROACH

PHASE 1--Reconnaissance

1. Determine algal species present in 2 or three streams in various watersheds in the Austin urban/suburban corridor.
2. Sample selected algal species (3 or 4) from each stream and measure nitrogen isotope in the biomass.
3. Sample and measure water chemistry and flow in streams, including major cations and anions, nutrients, field parameters, and nitrogen isotopes.
4. Determine principal land uses in watersheds and map using GIS coverages.

PHASE 2--One-year monitoring program

1. Select about 4 sites irepresenting single sources of nitrate, and one site that represents a composite of sources in each of two watersheds for the purposes of sampling nitrogen isotopes in algal growth, water chemistry and oxygen and nitrogen isotopes (NO3) (discharge-weighted composites) on a monthly basis, and measure stream discharge. From these results, fractionation factors for algal species uptake of nitrogen can be determined.
2. Measure nitrogen isotopic content and oxygen isotopic content of nitrate from all potential sources of nitrate to the stream, natural sources, fertilizers, sediment, animal wastes, sewage and septic tank effluents.
3. Identify algal feeders, both vertebrate and invertebrate (if present) from the sites, and sample, and analyze for nitrogen isotopic content.

BENEFITS

Results of this research has very high transfer value and can potentially lead to better use of algae as an integrator of water quality in streams, regarding elevated nitrate concentrations from potentially identifiable sources in a watershed. Further, the fractionation factor for nitrogen uptake by algal species can be measured and reported. The research provides the opportunity for geochemists and stream ecologists to enhance the understanding of the nitrogen biochemical cycle in watersheds. The results should be useful to City planners in evaluating sources of nutrient contamination to streams and water supplies as a result of current land use practices. Adverse impacts such as elevated nitrate may require greater controls on those specific land uses.